

Grain growth of ice from aqueous solutions of sugars, salts and amino acids

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Introduction

Salts and organic matters exist in icy bodies and comets. Chemical evolution from simple molecules to more complex organic compounds is a hot issue concerning the origin of life. Mixtures of ice and organic matters can play an important role for chemical evolution. Sugahara and Mimura (2015) conducted shock experiments on a mixture of alanine, ice, and silicate under cryogenic conditions simulating comet impacts and reported the oligomerization of alanine. For precise understanding of the reaction, it is necessary to observe morphology of ice including organic matters at low temperature. Effects of salts, amino acid and sugar to morphology and grain growth of ice are important research targets for food science as well as planetary science. In this study, we investigate grain-growth kinetics of ice crystallized from salt, sugar or amino-acid solutions from in-situ optical observations at low temperature.

Experimental procedure

Pure water, NaCl solutions, amino-acid (aspartic acid and glutamic acid) solutions and sugar (glucose, sucrose, maltose, maltotriose and maltotetraose) solutions were prepared as samples. These sample solutions were set between two cover glasses with a gap of ~40 μm on a heating-cooling stage and sample chamber was filled with dry nitrogen gas. These sample solutions were rapidly cooled to -30 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. After the samples were frozen, the sample temperature was increased at a rate of 10 $^{\circ}\text{C}/\text{min}$ and was kept for 300 min at -5 $^{\circ}\text{C}$. Optical images and movies were collected in situ under a polarizing microscope with crossed nicols. Phase identifications were conducted by Raman spectroscopy.

Results and Discussion

Figure 1 shows representative optical photographs of ices after 300 minutes reaching at -5 $^{\circ}\text{C}$. All solutions froze into aggregates of fine ice crystals in a moment before reaching at -30 $^{\circ}\text{C}$. In pure water, no homogenous grain growth was observed after 300 min at -5 $^{\circ}\text{C}$, but abnormal grain growth up to approximately 50 μm was observed. In the case of a salt solution, after reaching at -5 $^{\circ}\text{C}$, ice grains grew to a homogeneous size of 35 μm in average and the solution existed in triple junctions between ice crystals. In amino acid solutions, notable grain growth was not observed and fine grains remained. The abnormal grain growth similar to the case of pure water was observed in some cases of amino acids. Moreover, grain-growth rate in amino acid system was much lower than the case of pure water. This result suggests that amino acid inhibits grain growth of ice. In sugar solutions, when number of carbon ring changed from 2 to 4, appearances of samples changed drastically.

This study confirmed that morphology and grain-growth kinetics of ice are strongly affected by chemical composition of starting solutions. These results are useful to understand chemical reactions occurring in ice and will contribute to improve frozen preservation of foods.

Keywords: sugars, salts, amino-acids, grain growth, observation in situ

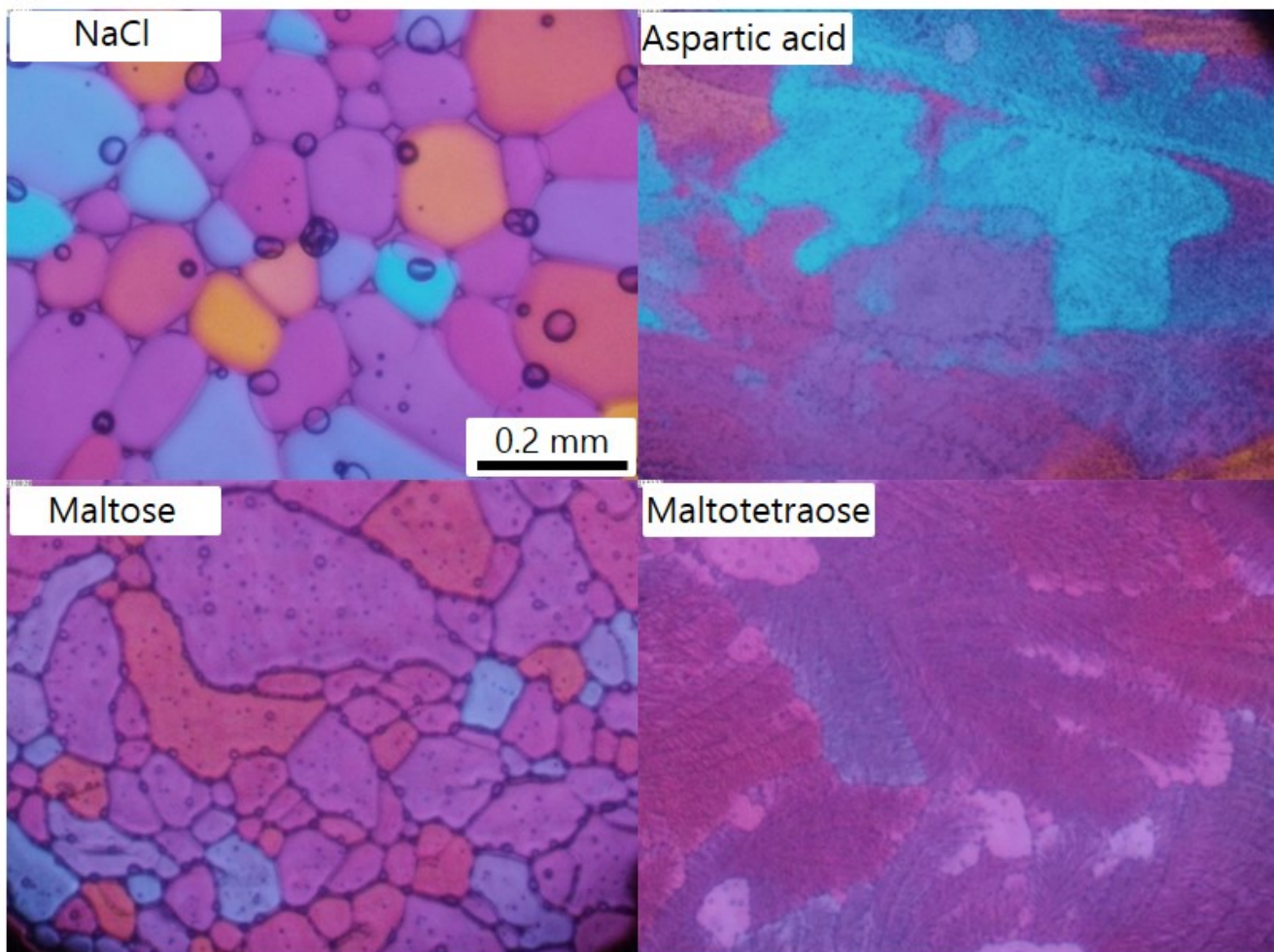


Figure 1. Representative optical images (crossed nicols) of ice crystals obtained 300 min after reaching at $-5\text{ }^{\circ}\text{C}$. The contrasts of these images depend on crystal orientations.

Reproduction of hysteresis in crystal growth

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Step dynamics is one of the fundamental physical processes of crystal growth. There are numerous steps with atomistic-scale heights on the crystal surface. A growth component such as an atom or molecule that lands on the surface usually migrates laterally until it reaches the steps -or until it desorbs into the mother phase. A growth component that reaches a step becomes incorporated into the crystal, leading to advancement of the step. Every passages of the steps increase the height of the surface by a monolayer (layer-by-layer growth). Therefore, the understanding of what determines the generation of steps and the rate of the advancement is essential to elucidate the crystal growth mechanism.

The step dynamics is significantly affected by the existence of impurities. The growth hysteresis is one of the well-known phenomena induced by impurities [e.g., 1]. Let us consider the crystal growth from aqueous solution. When the solution includes impurities, the crystal growth rate when the supersaturation is increased is different from that when it is decreased. It has been considered that the hysteresis results from the interaction between two effects: (i) retardation of the step advancement by impurities adsorbed on the crystal surface, and (ii) prevention of the impurity adsorption by frequent step passages. In previous theories of the growth hysteresis, the physical quantities such as the density of adsorbed impurities and the step velocity were averaged both in space and time (mean-field theory [e.g., 2-4]). However, these quantities differ from the position to position on the crystal surface and vary with time in actual situations, so it was not obvious whether the mean-field theory is applicable to the actual systems or not.

In this meeting, we report the results of the numerical simulations of growth hysteresis, which was recently accepted for publication in *Crystal Growth and Design* [5]. Recently, we have developed a new numerical scheme to simulate the step dynamics based on a phase-field (PF) method [6,7]. We introduced the adsorption/desorption processes of impurities to this method based on the Monte Carlo (MC) method in order to simulate the random impurity adsorption and its time variation. We investigated the change in the step velocity during down-and-up cycles of supersaturation, and found that the appearance of the growth hysteresis in all cycles. The average trace of the step velocity agreed with that predicted by the mean-field theory [3]. This is the first result that reproduces the growth hysteresis using the numerical simulations.

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Keywords: Crystal growth, Step dynamics, Impurity, Hysteresis

Numerical calculation of montmorillonite dissolution in consideration of the size distribution

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In recent years, how to dispose of large amounts of radioactive waste that were generated with the use of nuclear power plants has become an issue. In Japan, a geological disposal has been studied as one of the feasible disposal methods. In the geological disposal, the high-level radioactive waste in glass solidified body is placed in a steel container, then covered with a cushioning material mainly composed of clay minerals (montmorillonite) of bentonite, and it is disposed of the underground deeper than several hundred meters. Montmorillonite expands in contact with water and therefore it has a function to protect the radioactive waste from groundwater. However, during a long period spanning several thousand years, the reaction with the groundwater causes the dissolution of montmorillonite, so there is a risk that the radioactive material of the inside is flowing out by groundwater. Therefore, it is very important to predict the dissolution behavior of montmorillonite for the long-term stability of storage.

In the present study, we carried out the numerical calculation in order to examine the dissolution behavior of montmorillonite. We assumed that montmorillonite particles with various sizes are exposed to the alkaline solution under closed environment. The size change of each particle by dissolution and the concentration change of the solution were calculated. We considered that the dissolution rate depends on the degree of supersaturation of the solution, and the particle size (Gibbs-Thomson effect). When the solution is unsaturated, the dissolution rate is given by an empirical formula obtained by dissolution experiments [1]. When the solution becomes supersaturated, we assumed that the montmorillonite particles are turned to growth and the growth rate is given by the same form to the dissolution rate except of its sign. The degree of saturation of the solution was calculated by using the PHREEQC [2]. As the initial particle size distribution, we examined the following four cases: uniform, log-uniform, normal and log-normal distributions. Let us describe the numerical results of the case that the initial size distribution is log-normal. At the beginning of the calculation, all sizes of particles are dissolved in the unsaturated solution. The particle dissolution increases the degree of supersaturation, and eventually the solution becomes supersaturated. The small particles continue to be dissolved by the Gibbs-Thomson effect, however, the larger particles are turned to growth. The period that is required for the larger particles begin to grow depended on the ratio of the total particle volume to the solution volume (solid-liquid volume ratio) at the beginning of the calculation. In the case of the solid-liquid volume ratio is 10^{-5} , the larger particles are turned to growth after about 7000 years. With increasing the solid-liquid volume ratio, it was found that the period is reduced to about 10 to 100 years. It was also found that the lower limit of the size above which the montmorillonite particles are turned to growth increases with increasing the solid-liquid volume ratio. Thus, by the numerical calculation of the dissolution process of the different-sized montmorillonite particles, we concluded that it is important to consider the Gibbs-Thomson effect for the long-term stability of storage.

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Nucleation experiment of alumina and silica from vapor phase using the sounding rocket S-520-30

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Nucleation event determines the condensation sequence, number density, size, morphology and crystalline structure of cosmic dust particle, called dust, in a gas outflow of dying stars or a gas plume after shock wave heating in the primitive solar nebula. Using nucleation theories, such characters of dust have been expected. However, it has been well known that results obtained by classical nucleation theory and by experiments have a large difference each other. We believe that one of the reasons is the difference of physical parameters of nanometer sized particles from its bulk. Although nucleation is a process progressed in nanometer scale, physical parameters of bulk materials have been used. To determine the physical parameters of nanoparticles, we constructed an in-situ observation system of temperature and concentration during homogeneous nucleation in vapor phase using interferometry in the laboratory.

Nanoparticles are formed as dust analogues from a supersaturated vapor after evaporation of the starting material by electrical heating in a gas atmosphere. Using the specially designed double-wavelength Mach-Zehnder-type laser interferometer, nucleation temperature and partial pressure can be obtained simultaneously. Then, surface free energy and sticking probability can be determined using timescale for cooling based on nucleation theories (Kimura et al. 2012). In case of laboratory experiment, convection of gas atmosphere caused by thermal heating generates heterogeneity of nucleation environment, such as temperature and concentration profiles around evaporation source. In microgravity, evaporated vapor diffuses uniformly and the temperature profile becomes concentric around the evaporation source. As the result, nucleation will occur at the same condition. In addition, microgravity condition allow us to duplicate the ratio of timescale for cooling and collision frequency of vapor around supernovae and asymptotic giant branch stars. Therefore, we performed microgravity experiments using the sounding rocket S-520-30 launched on September 11th, 2015.

Two same experimental systems, which construct with the interferometer, nucleation chamber and camera recording modules were designed to fit the size and weight limitation and installed into the nosecone of the rocket. The evaporation source and gas atmosphere are silica and argon (4×10^4 Pa) for silica dust, and alumina and a gas mixture of oxygen (2×10^3 Pa) and argon (3.8×10^4 Pa) for alumina dust. The experiments were run sequentially and automatically started after launch of the rocket. The evaporation sources of silica and aluminum were electrically heated in the gas atmosphere under microgravity. Evaporated vapor was diffused, cooled and nucleated in the gas atmosphere. The temperature and concentration at the nucleation site can be determined from the movement of the interference fringes. Here, we will show the results of the experiments including supersaturation ratio, and the physical properties of those nanoparticles.

Keywords: Microgravity, Dust, Nucleation

Visualization of pH change around calcium carbonate crystals during dissolution and growth

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For the investigation of the growth and dissolution of calcium carbonate, CaCO_3 , it is important to understand how carbonate and bicarbonate ions behave in these processes. The pH monitoring of a solution during CaCO_3 growth or dissolution is a useful technique for this purpose, and actually in a number of the previous studies, the pH measurements of bulk solution during the growth have been performed. However, to clarify the detail process on the surface, especially the behavior of bicarbonate ions, regional change of pH just above the crystal surface should be monitored. Recently, we have started an attempt to visualize the distribution of pH around CaCO_3 crystals which inorganically grows or dissolves, by applying the method used for the research on the biogenic calcification of foraminifers. We have succeeded to detect the pH change near a dissolved calcite surface, which may provide new insights into both inorganic and biogenic formation mechanism of CaCO_3 .

Keywords: calcium carbonate, dissolution, pH

Crystal growth in clay solidification: zeolitization of smectite

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At the Earth's surface, rock-forming minerals are weathered and altered to be fine particles of clay. Though the clay particles stably exist in the burial condition, unconsolidated mud composed of clays is re-equilibrated with groundwater and diagenetically stabilized as solidified sedimentary rock. One of the most friendly clay material in our life is smectite. Since smectite under subsurface condition suffers from alkaline groundwater and can be altered into zeolite, the natural bentonite rocks composed of smectite always contain zeolite.

Investigating growth kinetics of zeolite at various solution, temperature and pressure conditions is important to estimate the time-scale of stabilization of clay materials. We conducted alteration experiment of Na-montmorillonite in 1.0 M NaOH at 120 °C and measured dissolution and growth rates by in-situ phase-shift interferometry [1]. The simplified reaction can be scripted as: $Al_2Si_4O_{10}(OH)_2 + 2NaOH = 2NaAlSi_2O_6(H_2O)$. At this condition, dissolution of montmorillonite proceeds at $6.9E-6$ m/s calculated from rate equation [2] and molar volume. Growth rate of analcime was measured to be $1.1E-10$ m/s. Since the reactive surface area of montmorillonite is reducible from 1/10 to 1/1000 by layer-stacking, this observed growth rate of analcime is mostly consistent. However, total volume change of before and after reaction gives $193.96 - 173.91 = +20.05$ cm³/mont mol, which suggests that this reaction is suppressed in the limited space. Further, reaction system in the presence of large excess NaOH with a syringe compaction cell produced zeolite as hydro-sodalite scripted as: $3Al_2Si_4O_{10}(OH)_2 + 20NaOH = Na_8Al_6Si_6O_{24}(OH)_2 + 6Na_2SiO_3 + 12H_2O$. Its volume change is calculated to be $+54.67$ cm³/mont mol, which suggests that this reaction can be more suppressed than low-alkaline system. Thus, alkali plays important role for stabilization by zeolitization but this alteration cannot be achieved entirely except at pores.

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[2] Sato et al. (2005) Proc. of the Int. Workshop on Bentonite-Cement Interaction in Repository Environments, A3-38-41.

Keywords: smectite, zeolitization, growth rate, volume change